

(19) World Intellectual Property Organization  
International Bureau(43) International Publication Date  
14 December 2000 (14.12.2000)

PCT

(10) International Publication Number  
WO 00/75496 A1(51) International Patent Classification<sup>7</sup>:

F01N 3/28

(74) Agents: SZYMANSKI, Brian, E. et al.; 3M Innovative Properties Company, Office Of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

(21) International Application Number: PCT/US99/23537

(22) International Filing Date: 8 October 1999 (08.10.1999)

(81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:  
09/328,065 8 June 1999 (08.06.1999) US

(71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

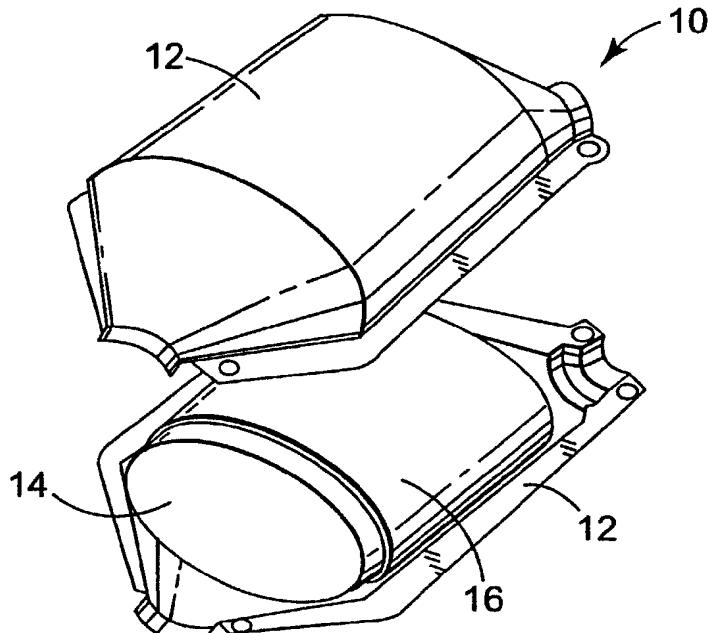
(72) Inventor: LANGER, Roger, L.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US).

Published:

— With international search report.

[Continued on next page]

(54) Title: HIGH TEMPERATURE MAT FOR A POLLUTION CONTROL DEVICE



(57) Abstract: A high temperature mat (16) for a pollution control device (10). The high temperature mat is generally utilized in pollution control devices (10) such as catalytic converters (14) and diesel particulate filters. The mat (16) includes a mixture of polycrystalline fibers and annealed ceramic fibers. The polycrystalline fibers are generally sol-gel formed fibers that do not contain any ceramic particulate matter. The other ceramic fiber component of the present invention is an annealed ceramic fiber. The combination of the noted fibers results in a high temperature mat (16) having desirable resiliency value and good erosion resistance at high temperatures and normal mounting pressures. The high temperature mat is suitable for use as an insulating layer in an end cone of a pollution control device (10) or for wrapping a pollution control element (14) and securing the wrapped element within the pollution control device (10).

WO 00/75496 A1



*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## HIGH TEMPERATURE MAT FOR A POLLUTION CONTROL DEVICE

The present invention relates to mounting materials for pollution control devices, and more particularly to a sheet of mounting material suitable for as a high temperature insulating layer in a pollution control device, and even more particularly to a sheet of mounting material containing a mixture of polycrystalline fibers and annealed ceramic fibers.

### Background

10       Pollution control devices are employed on motor vehicles to control atmospheric pollution. Catalytic converters and diesel particulate filters are two types of pollution control devices which are currently in widespread use. Both of these devices typically contain a pollution control element, or monolithic structure, mounted within a metal housing with a mounting material disposed between the structure and the walls of the 15      housing. The monolithic structure, or monolith, is either made from metal or more commonly, a ceramic material. In a catalytic converter, the monolith supports a catalyst which promotes the oxidization of carbon monoxide and hydrocarbons, and the reduction of oxides of nitrogen at high temperatures, e.g., over 260°C. Diesel particulate filters or traps are wall flow filters which have honeycombed monolithic structures typically made 20      from porous crystalline ceramic materials.

25       Ceramic monoliths generally have very thin walls and are susceptible to breakage. Typically, a ceramic monolith has a coefficient of thermal expansion about an order of magnitude less than the metal housing in which it is contained. To avoid damage to the ceramic monolith from road shock and vibration, to compensate for the differences in thermal expansion of the monolith and housing, and to prevent exhaust gases from flowing 30      between the monolith and metal housing, mounting materials are typically disposed between the ceramic monolith and the metal housing.

The process of placing or disposing of the mounting material or mat is also called canning and includes such processes as injecting a paste into a gap between the monolith and the metal housing, or wrapping a sheet or mat material around the monolith and inserting the wrapped monolith into the housing. Mats are generally made with various

types of ceramic fibrous materials. The ceramic fibers are made by conventional processes, such as melt-forming processes.

A sol-gel process is another method utilized for providing fibers for use in mounting mats. The sol-gel process produces fibers that are generally characterized with high temperature resiliency and a desirable level of erosion resistance. However, fibers produced from the sol-gel process typically have a low density that requires additional processing in order to provide a mat suitable for direct application in a pollution control device. Additionally, the economic costs of operating a sol-gel process can be quite high in comparison to other conventional fiber producing processes.

10

#### Summary

The present invention is directed to a high temperature mat for a pollution control device. The mounting mat is suitable for wrapping a pollution control element and securing the wrapped element within the pollution control device. Additionally, the high temperature mat can be utilized as an insulating layer in a double wall end cone of a pollution control device. The present invention is generally utilized in pollution control devices such as catalytic converters and diesel particulate filters.

15

The high temperature mat of the present invention includes a mixture of polycrystalline fibers and annealed ceramic fibers. The polycrystalline fibers are generally sol-gel formed fibers that contain very small amounts of (or less than 5% by weight of) any ceramic particulate matter. The other ceramic fiber component of the present invention is an annealed ceramic fiber that has at least partial crystallinity. The combination of the noted fibers results in a mounting mat having a density that is suitable for direct use in pollution control devices without requiring additional processing steps. The present mounting mat also has good erosion resistance and a desirable resiliency value at high temperatures and normal mounting pressures.

20

The high temperature mat is utilized in pollution control devices. A pollution control device of the present invention includes a housing and a pollution control element positioned within the housing. A mounting mat, produced in accordance with the present invention, is positioned around the outer surface of the element between the element and the housing. Alternatively, the high temperature mounting mat can be utilized as an insulating layer in a double wall end cone of a pollution control device -- i.e., the

insulating layer is sandwiched between inner and outer metal cone of a double wall end cone.

It is an advantage to provide a mounting mat that has a desirable density and bulk thickness that does not require additional processing to achieve a desired bulk density prior to canning. It is also an advantage to provide a pollution control device utilizing the high temperature mat to obtain a desirable resiliency and good erosion resistance at elevated operating temperatures and normal mounting pressures .

For purposes of the present invention, the following terms used in this application are defined as follows:

10 "shot-free ceramic fibers" polycrystalline fibers having less than about 5% particulate ceramic material and are typically formed by the sol-gel process;

"annealed amorphous fibers" means melt formed refractory ceramic fibers that have been that have been annealed to a temperature sufficient to improve the resiliency of the fibers. Preferably, the annealing process is stopped before the fibers become excessively friable as determined by the cold erosion test. The annealed fibers exhibit a degree of crystallinity as determined by X-ray diffraction and by transmission electron microscopy for microcrystallinity. Suitability of fibers can be determined by differential thermal analysis;

20 "resiliency" means the ability to maintain substantial holding force despite repeated thickness change. i.e., compression and relaxation cycles; and

"ceramic-based fibers" means fibers containing an amount of metal oxides, metal carbides, metal nitrides, or combinations thereof at levels of 80% or greater.

#### Brief Description of the Drawings

25 The invention will be more fully appreciated with reference to the following drawings in which similar reference numerals designate like or analogous components throughout and in which:

FIG. 1 is an exploded perspective view of a wrapped pollution control element positioned within a housing.

30 FIG. 2 is a segmented view of a two layered sheet of mounting material according to the present invention;

FIG. 3 is an X-ray diffraction diagram of a melt-formed ceramic fiber containing a crystalline structure; and

FIG. 4 is an X-ray diffraction diagram of a melt-formed ceramic fiber exhibiting a non-crystalline structure.

5

Detailed Description

FIG. 1 depicts a pollution control device 10 utilizing the mounting material of the present invention. The pollution control device 10 includes a housing 12 and a pollution control element 14. The pollution control element 14 is resiliently supported by a high temperature mounting mat 16. The material utilized for the mounting mat 16 includes a combination of polycrystalline ceramic fibers and annealed ceramic fibers.

The mounting material of the present invention is particularly useful for thin-walled ceramic monoliths and metallic monoliths where a high degree of resiliency provides the force required to keep the pollution control element, or monolith in place.

15 Surprisingly, the combination of polycrystalline ceramic fibers and annealed ceramic fibers provide a high degree of resiliency and erosion resistance with decreased shrinkage while maintaining adequate pressure retention at the operating temperatures of a pollution control device.

20 The mats made from the combination of materials of the present invention provide an advantage over mats formed in their entirety from either pure polycrystalline fibers or annealed ceramic fibers or a combination of polycrystalline fibers and ceramic fibers that have not been annealed. Mats which are formed from all polycrystalline fibers generally have an undesirable low density. Additionally, all polycrystalline fiber mats are bulky and must be compressed substantially, e.g., by a factor of about 10 to achieve the desired 25 mount density needed to generate sufficient holding force to keep a monolith in place. Additionally, the mats made from polycrystalline materials must be compression bonded by means such as needle stitching, enclosing in a bag, adding binder and drying or curing under pressure to maintain the desired amount of compression, or combinations thereof to facilitate canning. Mats produced using only annealed fibers tend to exhibit lower 30 resiliency values and reduced pressure retention values. The mats of the invention can be canned easily without additional compression means to hold the fibers down.

Additionally, mats utilizing the combined fibers of the invention have both desirable resiliency values and pressure retention values.

In accordance with the present invention, the mounting material is generally provided in the form of a mat or sheet of material. The mat can be a single layer or 5 multiple layers of the combined fibers. In one embodiment, a mat comprising a mixture of polycrystalline fibers and annealed ceramic fibers is used to mount the monolith. In another embodiment, a mat is formed of polycrystalline fibers, annealed ceramic fibers, and one or more intumescent materials. In yet another embodiment, a mat is formed comprising a layer of a mixture of polycrystalline fibers and annealed ceramic fibers, and 10 one or more other layers, any of which can include intumescent materials. FIG. 2 depicts an example of the latter embodiment of a mat 20 having a first layer 22 of a mixture of polycrystalline fibers and annealed ceramic fibers and a second layer 24 of ceramic fibers which includes intumescent materials. Preferably, the first layer 22 of fibers is mounted against the monolith.

15 The ceramic-based polycrystalline fibers suitable for use in the present invention are generally produced from conventional sol-gel production processes. The use of polycrystalline fibers imparts a high temperature resiliency and erosion resistance to the mat of the present invention. Additionally, the utilization of a sol-gel process results in shot-free fibers. Fibers which contain shot, or particulate matter, can adversely impact the 20 strength of the mat. Polycrystalline fibers useful in forming the mounting mat are those commercially available under the tradenames Nextel Fiber 312, Nextel Fiber 440, Nextel Fiber 550 all from 3M Company of St. Paul, MN, Fibermax fiber from Unifax of Niagara Falls, NY, Saffil fiber ICI Americas of Wilmington, DE, and Maftec fiber from Mitsubishi Chemical Corp. of Tokyo, JP. Preferably, the fibers contain a high amount of alumina. 25 Most preferably, the alumina content is 60% or greater. The fibers compositions can also contain an amount of silica or zirconia. The length and diameter of the polycrystalline fibers can vary for particular applications. However, the polycrystalline fibers generally have fiber lengths greater than 5 cm and fiber diameters between about of 2 to 12 microns.

30 Annealed ceramic fibers are utilized in combination with the polycrystalline fibers to impart desirable properties to the finished mat. The annealed ceramic fibers are generally melt-formed refractory ceramic fibers which can be melt-blown or melt-spun from a variety of metal oxides. The melt-formed refractory fibers are subsequently

annealed or heat treated at a temperature dependent upon the composition to form annealed amorphous fibers. The fibers are preferably a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  having from 30 to 60% by weight of alumina and from 60 to 40% by weight of silica, preferably about equal parts by weight. The mixture can include other oxides such as 5  $\text{B}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_5$ , and  $\text{ZrO}_2$ .

Melt-formed refractory ceramic fibers that can be used to make the high temperature mat are available from a number of commercial sources and include those known under the trade designation "Fiberfrax" from Unifrax., Niagara Falls, NY; "Cerafiber" and "Kaowool" from Thermal Ceramics Co., Augusta, GA; "Cer-wool" from 10 Premier Refractories Co., Erwin, TN; and "SNSC" from Shin-Nippon Steel Chemical of Tokyo, Japan. The manufacturer of ceramic fibers known under the trade designation "Cer-wool" states that they are melt-spun from a mixture of 48% by weight silica and 52% by weight alumina and have an average fiber diameter of 3-4 micrometers. The manufacturer of ceramic fibers known under the trade designation "Cerafiber" states that 15 they are meltspun from a mixture of by weight 54% silica and 46% alumina and have an average fiber diameter of 2.5-3.5 micrometers. The manufacturer of ceramic fibers "SNSC 1260-D1" states that they are melt-formed from a mixture of 54% by weight silica and 46% by weight alumina and have an average fiber diameter of about 2 micrometers.

The diameter of individual annealed ceramic fibers for the mat may vary 20 depending on specific end uses. Typically, the diameters range from about 2 to about 8 micrometers because larger or smaller diameter fibers are difficult to make by melt forming refractory processes. Larger diameter fibers could produce a mat that would be more fragile which may require more binder to afford adequate handleability. It is difficult to melt-form refractory ceramic fibers at diameters smaller than 2 micrometers or larger 25 than 8 micrometers.

The melt-formed refractory ceramic fibers must be annealed prior to end use 30 application. When melt-formed refractory ceramic fibers are annealed at high temperatures, e.g., over 850°C or higher, the fibers devitrify or change into a crystalline state. There is a transition point during the devitrification process in which some fibers may develop a microcrystalline structure that is not detectable by X-ray diffraction, but can be detected by transmission electron microscopy. Other fibers start to develop crystallinity that is detectable by X-ray diffraction.

The fibers suitable in the practice of the invention are those which have been annealed at a temperature at which the formation of crystals starts or higher. FIG. 3 shows an X-ray diffraction scan of fibers that have been annealed sufficiently for the invention. FIG. 4 depicts an X-ray diffraction scan of amorphous fibers that would not be suitable for use in the invention. Those skilled in the art are capable of determining the presence of crystallinity from X-ray diffraction scans or alternatively from transmission electron microscopy.

There exists a time-temperature relationship in which the fibers can be annealed. For example, the fibers can be annealed at lower temperatures for longer periods of time to cause the crystal formation, or they can be annealed for shorter times at high temperatures. A suitable annealing temperature for the melt-formed fibers can be determined by differential thermal analysis (DTA) using equipment such as that available from Seiko Instruments, Inc. Those skilled in the art are capable of utilizing DTA data to determine temperatures at which specific fibers must be heated in order to achieve a desired level of annealing. For example, fibers having an approximate composition of 50% alumina and 50% silica would have an optimum annealing temperature of about 1000°C as indicated through differential thermal analysis.

Preferably, the annealing time and temperature are controlled so that the fibers do not become friable and difficult to handle. Additionally, excessive heat and time are unnecessary to achieve the advantages of the invention. The temperature at which the devitrification starts may vary depending upon factors such as how quickly the temperature is raised in the DTA and the material composition, but the temperature is typically between about 850°C and 1050° C.

Preferably, the annealed ceramic fibers and polycrystalline fibers are combined and randomly mixed to provide the high temperature mat of the present invention. A useful mat can be made from about 5% to about 95% annealed ceramic fibers and 5 to 95% polycrystalline fibers wherein the sum of the weight of annealed ceramic fibers and the polycrystalline fibers is equal to 100%. Preferably, the mat is made from about 10 to 90% annealed amorphous fibers and 90 to 10% shot free ceramic fibers, and more preferably 20 to 80% annealed ceramic fibers and 80 to 20% polycrystalline fibers. It is preferred to minimize the amount of shot free fibers as these tend to be more costly to make and the larger amount of shot free fibers results in a mat that is more bulky. The annealed ceramic

fibers may be present as long as the amounts of these fibers do not reduce the Resiliency Value of the mat to below 10 kPa or lead to an excessive erosion rate. Additionally other fibers may be added as long as the Resiliency Value of the mat is above 10 kPa.

5        Optionally, the mats of the present invention can further include intumescent materials. Suitable intumescent materials include, but are not limited to unexpanded vermiculite, vermiculite ore, partially delaminated vermiculite, expandable graphite, hydrobiotite, water swellable synthetic tetrasilicic fluorine type mica described in U.S. Pat. No. 3,001,571 (Hatch), partially dehydrated vermiculite as described in U.S. Pat. No. 5,151,253 (Merry et al.) and alkali metal silicate granules as described in U.S. Pat. No. 10      4,521,333 (Graham et al.). Preferred intumescent materials include unexpanded vermiculite, i.e., vermiculite ore, and expandable graphite. The choice of the intumescent materials can vary depending upon the desired end use. For higher temperatures, e.g., above about 500°C., vermiculite materials are suitable since they start to expand at about 340°C. to fill the expanding gap between the expanding metal housing and the monolith in 15      a catalytic converter. For lower temperature use, e.g., below about 500° C., such as in diesel particulate filters, treated graphite may be preferred since it starts to expand at about 210° C. Treated vermiculites are also available; these expand at about 290° C. Blends of various intumescent materials can also be used.

20        Intumescent materials within a layer can be used in a range of between about 5 to about 75% by weight of the entire mat. In this embodiment, the annealed ceramic fibers and polycrystalline fibers are present in the amounts from about 10 to 70%. Optionally, a binder is present in amounts of from about 2 to 20%.

25        The mats of the invention are preferably made with binders to facilitate handling and to provide sufficient integrity and resiliency to bend around a monolith. The binders may be inorganic, such as clays and colloidal silica, or organic. Organic binders are preferred as they provide the requisite resiliency for handling the mat but burn off after the mat has been wrapped around a monolith and inserted into the metal housing of a pollution control device in a process referred to in the art as "canning". Organic binders can be used in amounts from about 2 to 20% by weight on a dry basis.

30        Suitable organic binder materials include aqueous polymer emulsions, solvent-based polymers, and 100% solids polymers. Aqueous polymer emulsions are organic binders polymers and elastomers in the latex form (e.g., natural rubber latices, styrene-

butadiene latices, butadiene-acrylonitrile latices, and latices of acrylate and methacrylate polymers and copolymers). Solvent-based polymeric binders can include a polymer such as an acrylic, a polyurethane, or a rubber-based organic polymer. The 100% solids polymers include natural rubber, styrene-butadiene rubber, and other elastomers.

5 Preferably, the organic binder material includes an aqueous acrylic emulsion. Acrylic emulsions are preferred because of their aging properties and noncorrosive combustion products. Useful acrylic emulsions include those commercially available under the trade designations "RHOPLEX TR-934" (a 44.5% by weight solids aqueous acrylic emulsion) and "RHOPLEX HA-8" (a 45.5% by weight solids aqueous emulsion of acrylic copolymers) from Rohm and Haas of Philadelphia, PA., under the trade designation "NEOCRYL XA-2022" (a 60.5% solids aqueous dispersion of acrylic resin) from ICI Resins US of Wilmington, Mass., and under the trade name Airflex™ 600BP DEV (55% by weight solids aqueous emulsion of theylene vinyl acetate acrylate terpolymer) from Air Products and Chemicals, Inc., Allentown, Pa.

10

15 Organic binder materials can also include one or more plasticizers. Plasticizers tend to soften a polymer matrix and can contribute to the flexibility and moldability of the sheet materials made from the composition.

20 Other additives may also be added to form the mat in amounts needed for their intended purposes. Such additives include defoamers, flocculants, surfactants, and the like. Strength enhancing agents may be included with the inventive composition. Strength enhancing agents include, for example, organic fibers, such as cellulose fibers or bi-component binder fibers, and inorganic fibers, such as glass fibers or micro-fiberglass.

25 The high temperature mat of the present invention can be prepared by conventional means such as air laying or papermaking processes. In the papermaking process, ceramic fibers are mixed with water and a binder to form a mixture or slurry that is less than 10% solids. The slurry is then flocculated with flocculating agent and drainage retention aid chemicals. Then, the flocculated mixture is placed onto a papermaking machine to be formed into a mat and dewatered. The mats or sheets may also be formed by vacuum casting the slurry or mixture with conventional papermaking equipment. The mats are 30 then dried in ovens or at room temperature. The dried mats are then cut by means such as stamping or die cutting into the desired shape. Alternatively, after formation of the mat, the mat can be stitch bonded, needle bonded, spray bonded, or subjected to a vacuum

bagging process to place the mat in further condition for specific end use applications. Such modifications to the mat, with or without binder, are accomplished through processes conventionally recognized by those skilled in the art.

5 The mats can be made in various thicknesses to accommodate end use requirements. These requirements include the type of monolith (e.g., thin-walled, metal, standard thickness wall), the gap thickness at room temperature, the mount density at room temperature, the gap thickness at elevated temperatures, the pressure exerted by the mat at elevated temperatures, and the tendency of the mat to shrink or expand at elevated temperatures. A typical mounting mat having annealed ceramic fibers and polycrystalline 10 fibers, but no intumescent materials, may range in thickness from about 1 to about 25 mm.

When an intumescent layer is included in a two layer mat construction, such as that depicted in FIG. 2, the intumescent layer can range in thickness from about 0.5 mm to 15.0 mm while the non-intumescent fiber layer can range from about 1 mm to about 15 mm. Multiple layers of mats can be formed in various combinations of intumescent and 15 non-intumescent layers. In a pollution control device, an intumescent layer would be oriented such that it would be in contact with a metal housing.

When a mat is formed from a combination of fibers and intumescent materials within the same layer, the typical thickness can range from about 1 to 25 mm.

Additionally, the mats of the invention may include inserts such as those disclosed 20 in U.S. Patent No. 5882608, or edge protectant materials such as that disclosed in EP 639700.

25 The resulting mat of the present invention exhibits a desirable resiliency as indicated through the resiliency value as determined by the RCFT test described below in the Examples section. The resiliency value is 10 kPa or greater, and preferably 15 kPa or greater at a room temperature starting pressure of 180 to 220 kPa. The pressure retention, described in the RCFT test described below, is typically greater than about 10% and 30 preferably greater than about 12%.

The mats of the invention also exhibit low shrinkage. The shrinkage value of a given mat is recorded at temperatures between 500°C and 1000°C as determined through the Thermal Mechanical Analyzer test described below in the Examples section. A large amount of shrinkage between these temperatures is undesirable because the mat can lose holding power and allow the monolith to move and become damaged. The mats of the

invention shrink about 5%, or less preferably, the mat shrinks about 3% or less and more preferably about 1% or less in order to maintain sufficient pressure retention to hold the monolith in place during repeated use.

5 The mat of the present invention exhibits a desirable resistance to erosion. The erosion resistance of the mat is generally about 0.1 gram/hour or less, as measured in accordance with the cold erosion test described in the Examples section.

10 The density of the resulting mat is generally within the range of about 0.1 to about 0.7 g/cm<sup>3</sup>. When compressed to a mount density of between 0.21 and 1.3 g/cm<sup>3</sup>, these mats have the ability to maintain a substantial holding force on the monolith in a catalytic converter despite the repeated gap change that occurs as the catalytic converter is heated and cooled.

15 The mat of the present invention is utilized to either wrap pollution control elements for placement in a pollution control device or as an insulating mat for end cones of a pollution control device. Suitable pollution control elements, also referred to as monoliths, are known in the art and include those made of metal or ceramic. The monoliths are used to support the catalyst materials for the converter. A useful catalytic converter element is disclosed, for example, in U.S. Pat. No. RE 27,747 (Johnson). Further, ceramic catalytic converter elements are commercially available, for example, from Corning Inc. of Corning, N.Y., and NGK Insulator Ltd. of Nagoya, Japan. For 20 example, a honeycomb ceramic catalyst support is marketed under the trade designation "CELCOR" by Corning Inc. and "HONEYCERAM" by NGK Insulator Ltd. Metal catalytic converter elements are commercially available from Emitec Co. of Germany.

25 Pollution control devices includes both catalytic converters and diesel particulate traps. Diesel particulate traps similarly include one or more porous tubular or honeycomb-like structures (having channels closed at one end, however) which are mounted by a thermally resistant material within a housing. Particulates are collected from exhaust gases in the porous structure until regenerated by a high temperature burnout procedure, which thermally taxes the mounting material. The mounting mat of the present invention can also be used in catalytic converters employed in the chemical industry which are 30 located within exhaust or emission stacks, and which also contain fragile honeycomb type structures to be protectively mounted.

Thus, the objects of the invention are accomplished by the present invention, which is not limited to the specific embodiments described above, but which includes variations, modifications and equivalent embodiments defined by the following claims.

5      **TEST METHODS**

**Real Condition Fixture Test (RCFT)**

The RCFT is used to measure the pressure exerted by a mounting material under conditions representative of actual conditions found in a catalytic converter during normal use. It also provides a measure of resiliency.

10      Two 50.8 mm by 50.8 mm heated platens controlled independently are heated to different temperatures to simulate the metal housing and monolith temperatures.

15      Simultaneously, the space or gap between the platens is increased by a value calculated from the temperature and thermal expansion coefficients of a typical catalytic converter. The temperatures of the platens and the gap change are presented in Table 1 below. The force exerted by the mounting material is measured by a Sintech ID computer controlled load frame with Extensometer (MTS Systems Corp., Research Triangle Park, N.C.).

20      The test is run for 3 cycles. During the first cycle, the organic binder burns out; during the second cycle pressure starts to level out at 900°C, and by the third cycle, the pressure has stabilized. The pressure retention (RCFT Pressure Retention in %) is determined by dividing the pressure at 900°C during the third cycle by the starting, i.e., before any cycles have been run, pressure at room temperature. The pressure in kiloPascals at 900°C in the third cycle is also recorded. This pressure is referred to as the Resiliency Value.

TABLE 1

Top Platen Temperature -°C	Bottom Platen Temperature -°C	Cumulative Gap Change – mm
25	25	0
50	25	0
100	30	0
150	33	0
200	35	0
250	38	0
300	40	0
350	45	0
400	50	0
450	60	0
500	70	0
550	85	+0.0127
600	100	+0.0254
650	125	+0.0381
700	150	+0.0508
750	185	+0.0762
800	220	+0.1016
850	325	+0.1651
900	430	+0.2286
900	480	+0.2667
900	530	+0.3048
850	502	+0.2921
800	474	+0.2794
750	445	+0.2540
700	416	+0.2286
650	387	+0.2159
600	358	+0.2032
550	329	+0.1905
500	300	+0.1778
450	275	+0.1651
400	250	+0.1524
350	210	+0.1270
300	180	+0.1016
250	155	+0.0889
200	130	+0.0762
150	95	+0.0508
100	60	+0.0254
50	43	+0.0127
25	25	0

Thermal Mechanical Analysis Test (TMA)

Expansion of a mat during heating is measured in this test. The test uses a Theta Dilatronic II Thermal Analyzer, Model MFE-715. In the test, an 11 mm diameter circle of the test mat is placed in a furnace and heated uniformly at a rate of 15°C per minute to 5 1000°C. A 7 mm quartz rod rests on top of the mat and the rod supports a 1350 gram weight. On heating, the mat may contract initially up to about 400°C or until the organic binder is burned out. As the sample is heated further, the mat starts to shrink. This displacement is measured and recorded as a function of mat temperature. The mat thicknesses at 500°C (T1) and at 1000°C (T2) are used to calculate the percent shrinkage 10 (% shrinkage = [(T1-T2)/T1] x 100).

Cold Erosion Test

This test is an accelerated test conducted under conditions that are more severe than actual conditions in a catalytic converter. It provides comparative data as to the erosion resistance of a mat mounting material. A test sample is cut into a square 15 measuring 2.54 cm by 2.54 cm, weighed, and mounted between two high temperature Inconel 601 steel plates using spacers to obtain a mount density of 0.400+-0.005 g/cm<sup>3</sup>. The test assembly is heated for two hours at 800°C and cooled to room temperature. The cooled test assembly is then positioned 3.8 mm in front of an air jet oscillating back and forth over the edge of the mat at 20 cycles per minute. This test is discontinued after 0.2 20 grams of material is lost or after 24 hours, whichever occurs first. The air jet impinges on the mat at a velocity of 305 meters per second. The erosion rate is determined by the weight loss divided by the time of the test and is reported in grams/hour (g/hr).

Examples 1-3 and C1-C6

25 Fibers as listed in Table 2 were formed into mats as follows. The fibers were added to water in a Waring Blender at slow speed for about 10 seconds to form a slurry of 0.4% to 0.6% solids. The slurry was transferred to a 12 liter beaker with 10% by dry weight of a 45.5% solids acrylic latex binder (Rhoplex HA-8 available from Rhom & Haas) and mixed with a propeller mixer. A sufficient amount of a 50% aqueous solution 30 of aluminum sulfate was added to adjust the pH to a range of from 4 to 6. Then 10 grams of a 0.1% solution of a flocculent (Nalco 7530) and about 0.2 grams defoamer

(Foammaster III available from Henkel) were added and mixed with a propeller mixer. Immediately after mixing, the slurry was poured into a sheet mold as described in U.S. Patent No. 5,250,269, dewatered, wet pressed, and then dried to form a mat. The mats were tested for Pressure Retention in the RCFT Test, and for shrinkage as determined by the TMA Test. Catalytic converters can be made by wrapping the mats of Examples 1-3 around a monolithic structure, inserting the wrapped monolith into a metal housing, and welding around the housing.

Ex	Table 2 Fibers	Mat Density g/cc	Shrinkage %	RCFT Pressure Retention %	Resiliency Value kPa	RCFT RT@ 1 <sup>st</sup> cycle KPa
1	75% amorphous fibers*, annealed 25% polycrystalline fibers**	0.19	0.8	14.1	27	191
2	50% amorphous fibers*, annealed 50% polycrystalline fibers**	0.16	1.0	19.7	37	188
3	87.5% amorphous fibers*, annealed 12.5% polycrystalline fibers**	0.21	0.8			
C1	100% amorphous fibers*, annealed	0.24	0.5	7.6	15	197
C2	100% amorphous fibers*	0.22	24.8	0	0	191
C3	75% amorphous fibers*** 25% polycrystalline fibers**	0.20	19.8	1.5	3	195
C4	50% amorphous fibers*** 50% polycrystalline fibers**	0.17	9.3	10.0	18	180
C5	100% polycrystalline fibers**	0.16	2.4	27.4	58	212
C6	100% amorphous fibers***	0.32	25.9	0	0	190

\*Kaowool™ HA available from Thermal Ceramics

10      \*\*Saffil™ OBM available from ICI

\*\*\*Fiberfrax™7000M available from Unifrax

The data in Table 1 show the decreased shrinkage in the mats of the invention while having good pressure retention in the RCFT test.

5 Mats from Examples 1, 2, C1, and C5 were tested for cold erosion at a mount density of 0.4 g/cc. Data are shown in Table 3.

Table 3	
Example	Cold Erosion – g/hr @ 0.4 g/cc mount density
1	0.023
2	0.004
C1	0.127
C5	0.001

The data in Table 3 show the improvement in cold erosion of the mats of the invention over amorphous annealed fibers alone. While Example C5 had comparable erosion resistance, it would still require an undesirable compression bonding step prior to 10 final use.

#### Examples 4-6

The mats of Examples 1-3 are combined with an intumescent mat such as Interam™ Type 100 mat available from 3M Company to produce two layer mats each of 15 which has an intumescent layer and a non-intumescent layer. Catalytic converters are prepared by mounting the two layer mats between the monolith and the metal housing with the non-intumescent layer against the monolith and the intumescent layer against the housing. Optionally, the intumescent layer can be mounted against the monolith.

In Example 7, an intumescent material is combined with the ceramic-based 20 polycrystalline fibers and annealed fibers of Example 1. Unexpanded vermiculate flakes are added to the fibers of Example 1 in amount to obtain 30% by weight of material. The resulting mat would have a density within the range of 0.1 to 0.7 grams/cm<sup>3</sup>.

From the above disclosure of the general principles of the present invention and the preceding detailed description, those skilled in this art will readily comprehend the various 25 modifications to which the present invention is susceptible. Therefore, the scope of the invention should be limited only by the following claims and equivalents thereof.

**WHAT IS CLAIMED IS:**

1. A high temperature mat for use in a pollution control device, said mat comprising a mixture of ceramic-based polycrystalline fibers and annealed ceramic fibers.

5

2. A high temperature mat as recited in claim 1, wherein said mounting mat includes an organic binder.

3. A high temperature mat as recited in claim 1, wherein said ceramic-based polycrystalline fibers and said annealed ceramic fibers are bound in a fiber mass through either stitch bonding, needle bonding, spray bonding or vacuum bagging.

10 4. A high temperature mat as recited in claim 1, wherein said mat includes intumescent materials.

15

5. A high temperature mat as recited in claim 1, further comprising a layer of intumescent material bonded to said high temperature mat.

20 6. A high temperature mat as recited in claim 5, wherein said layer of intumescent material is either laminated onto a surface of said mat or co-formed with said mat.

7. A high temperature mat as recited in claim 1, wherein said ceramic-based polycrystalline fibers are included in a range of about 5% to about 95%.

25 8. A high temperature mat as recited in claim 1, wherein said annealed ceramic fibers are included in a range of about 5% to about 95%.

9. A high temperature mat as recited in claim 1, wherein said ceramic-based polycrystalline fibers contain alumina in an amount of about 60% or greater.

30

10. A high temperature mat as recited in claim 1, wherein said high temperature mat exhibits a resiliency value of about 10 kPa or greater according to the real condition fixtures test.
- 5 11. A high temperature mat as recited in claim 1, wherein a plurality of layers of said high temperature mat are bonded together.
12. A high temperature mat as recited in claim 1, wherein said high temperature mat exhibits shrinkage of about 5% or less.
- 10 13. A high temperature mat as recited in claim 1, wherein said high temperature mat exhibits a pressure retention of about 10% or greater.
- 15 14. A high temperature mat as recited in claim 1, wherein said high temperature mat has a density within the range of about 0.1 to about 0.7 g/cm<sup>3</sup>.
15. A high temperature mat as recited in claim 1, wherein said mat exhibits an erosion value of 0.1 g/hr or less in accordance with the cold erosion test.
- 20 16. A pollution control device, comprising:
  - (a) a housing;
  - (b) a pollution control element positioned within said housing, said pollution control element having an outer surface; and
  - (c) a high temperature mat as recited in claim 1 positioned around the outer surface of said pollution control element between said pollution control element and said housing.
- 25 17. A pollution control device as recited in claim 16, wherein said high temperature mat includes an organic binder.
- 30 18. A pollution control device as recited in claim 16, wherein said ceramic-based polycrystalline fibers and said annealed ceramic fibers are bound in a fiber mass through either stitch bonding, needle bonding, spray bonding, or vacuum bagging.

19. A pollution control device as recited in claim 16, wherein said mat includes intumescent materials.

5 20. A pollution control device as recited in claim 16, further comprising a layer of intumescent material bonded to said mounting mat, said mounting mat positioned against the outer surface of said pollution control element.

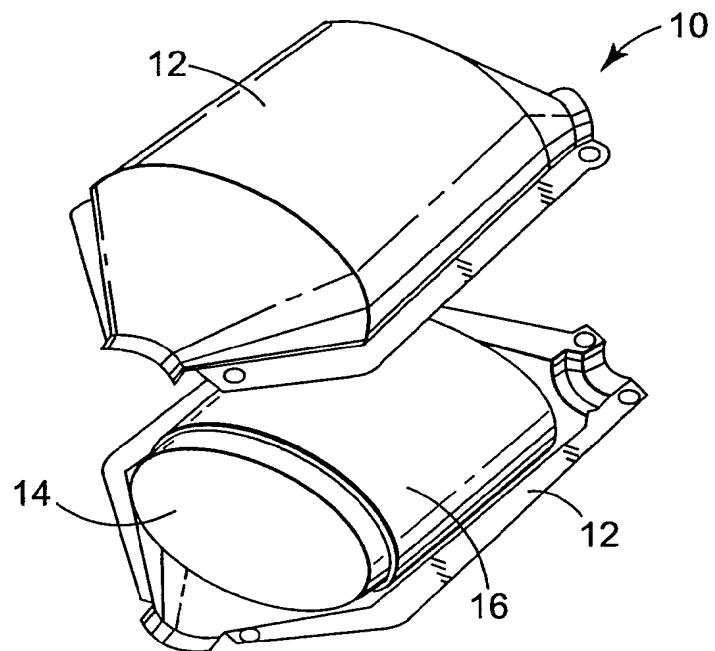
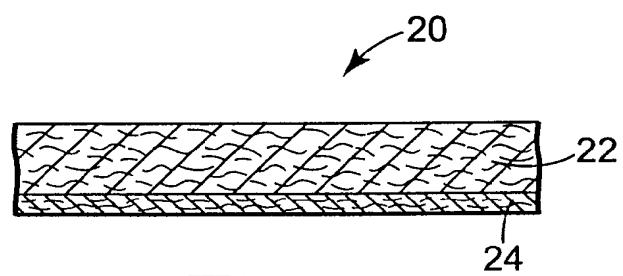
10 21. A pollution control device as recited in claim 16, wherein said polycrystalline fibers are included in a range of about 5% to about 95%.

22. A pollution control device as recited in claim 16, wherein said ceramic fibers are included in a range of about 5% to about 95%.

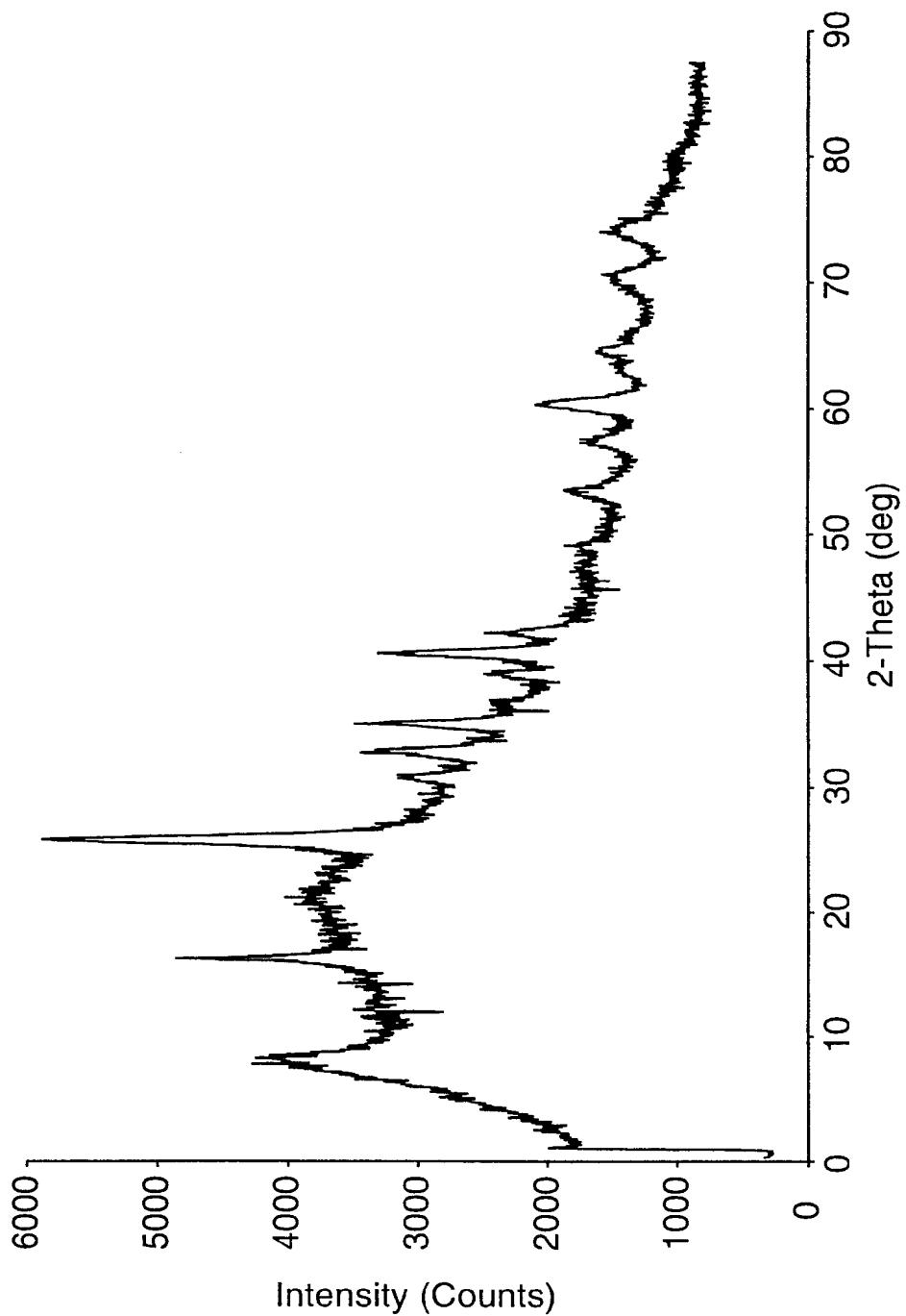
15 23. A pollution control device, comprising:

- (a) a housing having at least one double wall end cone; and
- (b) a high temperature mat as recited in claim 1 positioned between inner and outer cones of the double wall end cone of said housing.

1/3

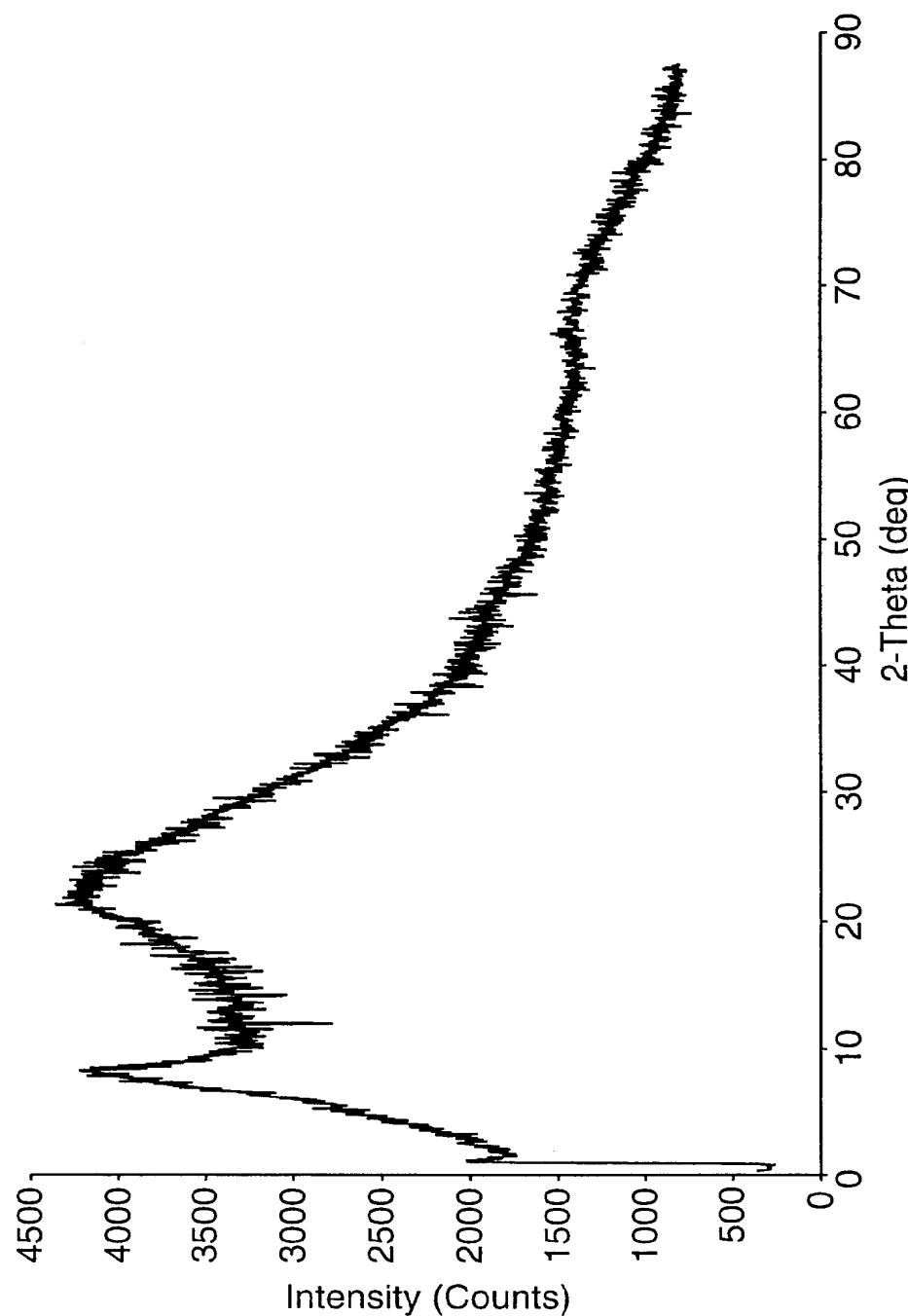
**Fig. 1****Fig. 2**

2/3



**Fig. 3**

3/3



**Fig. 4**

# INTERNATIONAL SEARCH REPORT

Int'l Application No	PCT/US 99/23537
----------------------	-----------------

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F01N3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 35144 A (SANOCKI STEPHEN M ;HOWORTH GARY F (US); LANGER ROGER L (US); MINNE) 13 August 1998 (1998-08-13) the whole document ---	1,2,4, 16,17,19
Y		3,18
A	US 4 929 429 A (MERRY RICHARD P) 29 May 1990 (1990-05-29) the whole document ---	1,2,4-6, 16,17,19
Y		3,18
A	EP 0 573 834 A (MINNESOTA MINING & MFG) 15 December 1993 (1993-12-15) the whole document ---	1,2,4, 10,16, 17,19
A	US 5 332 609 A (CORN STEWART H) 26 July 1994 (1994-07-26) ---	1,16
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

### Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

22 December 1999

18/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Tatus, W

## INTERNATIONAL SEARCH REPORT

international Application No  
PCT/US 99/23537

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 481 133 A (BABCOCK & WILCOX CO) 27 July 1977 (1977-07-27) the whole document ---	1,16
A	EP 0 366 484 A (MINNESOTA MINING & MFG) 2 May 1990 (1990-05-02) the whole document ---	1,4,16, 19
A	EP 0 856 646 A (CORNING INC) 5 August 1998 (1998-08-05) column 4, line 27 -column 4, line 48 -----	1,16

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/23537

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO 9835144	A 13-08-1998	AU 6244398	A	26-08-1998
US 4929429	A 29-05-1990	AU 2771889	A	17-08-1989
		CA 1311690	A	22-12-1992
		EP 0328293	A	16-08-1989
		JP 1240715	A	26-09-1989
		JP 2804280	B	24-09-1998
		KR 141603	B	01-07-1998
		MX 166513	B	13-01-1993
		US 5028397	A	02-07-1991
EP 0573834	A 15-12-1993	US 5250269	A	05-10-1993
		CA 2095777	A	22-11-1993
		DE 69302216	D	23-05-1996
		DE 69302216	T	05-12-1996
		JP 6033755	A	08-02-1994
US 5332609	A 26-07-1994	DE 9404954	U	28-07-1994
		GB 2276333	A	28-09-1994
		JP 7004234	A	10-01-1995
GB 1481133	A 27-07-1977	AR 204579	A	12-02-1976
		AU 8121675	A	18-11-1976
		BE 829069	A	01-09-1975
		BR 7502989	A	20-04-1976
		CA 1037973	A	05-09-1978
		DE 2521613	A	04-12-1975
		FR 2272968	A	26-12-1975
		JP 1271412	C	25-06-1985
		JP 51002714	A	10-01-1976
		JP 59005539	B	06-02-1984
		SE 408167	B	21-05-1979
		SE 7505057	A	01-12-1975
EP 0366484	A 02-05-1990	US 5008086	A	16-04-1991
		AU 614428	B	29-08-1991
		AU 4238689	A	03-05-1990
		CA 1326455	A	25-01-1994
		DE 68913270	D	31-03-1994
		DE 68913270	T	29-09-1994
		ES 2050814	T	01-06-1994
		KR 9502843	Y	15-04-1995
		MX 166480	B	12-01-1993
EP 0856646	A 05-08-1998	JP 10305231	A	17-11-1998
		US 5943771	A	31-08-1999